OFFICE OF NAVAL RESEARCH

Contract N00014-87-K-0531

R & T Code 431a016

TECHNICAL REPORT NO. 3

Hardening and Toughening of ZnS-Ga_2S_3 Ceramics by Solid-State Reactions

by

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Prepared for Publication in

Proceedings of the 5th European Electromagnetic Windows Conference
September, 1989, Toulon, France

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Los Angeles, California 90024

October 1, 1989

SECURITY CLASSIFICATION OF THIS PAGE

REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION Unclassified	1b. RESTRICTIVE MARKINGS
2a. SECURITY CLASSIFICATION AUTHORITY 2b. DECLASSIFICATION / DOWNGRADING SCHEDULE	3. DISTRIBUTION / AVAILABILITY OF REPORT Approved for public release: Distribution Unlimited
4. PERFORMING ORGANIZATION REPORT NUMBER(S) No. 3	5. MONITORING ORGANIZATION REPORT NUMBER(S) N00014-87-K-0531
6a. NAME OF PERFORMING ORGANIZATION University of California Los Angeles/Bruce Dunn 6b. OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION Office of Naval Research Dr. R. Schwartz
6c. ADDRESS (City, State, and ZIP Code) Department of Materials Science & Engineering University of California, Los Angeles 90024-1595	7b. ADDRESS (City, State, and ZIP Code) Code 38504 Naval Weapons Center China Lake, CA 93555
8a. NAME OF FUNDING / SPONSORING ORGANIZATION 8b. OFFICE SYMBOL (If applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER
8c. ADDRESS (City, State, and ZIP Code)	10. SOURCE OF FUNDING NUMBERS PROGRAM ELEMENT NO. / PROJECT NO. / TASK NO. / WORK UNIT NO.

11. TITLE (Include Security Classification)
Hardening and Toughening of ZnS - Ga_2S_3 Ceramics by Solid-State Reactions

12. PERSONAL AUTHOR(S)
A. J. Ardell, B. Dunn, W. W. Chen and J. Zhang

13a. TYPE OF REPORT	13b. TIME COVERED	14. DATE OF REPORT (Year, Month, Day)	15. PAGE COUNT
Technical	FROM 9/88 TO 9/89	1989, October 1	8

16. SUPPLEMENTARY NOTATION
Submitted to 5th European Electromagnetic Windows Conference

17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
FIELD	GROUP	SUB-GROUP	

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

ABSTRACT

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20. DISTRIBUTION / AVAILABILITY OF ABSTRACT ☐ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT ☐ DTIC USERS	21. ABSTRACT SECURITY CLASSIFICATION Unclassified
22a. NAME OF RESPONSIBLE INDIVIDUAL	22b. TELEPHONE (Include Area Code) / 22c. OFFICE SYMBOL

DD FORM 1473, 84 MAR — 83 APR edition may be used until exhausted. All other editions are obsolete.

SECURITY CLASSIFICATION OF THIS PAGE

HARDENING AND TOUGHENING OF $ZnS-Ga_2S_3$ CERAMICS BY SOLID-STATE REACTIONS

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ABSTRACT

We report here the first results of our research on the hardness and toughness of ZnS containing 16 mol % Ga_2S_3, which is the eutectoid composition. Hot-pressed material of 97 to 99 % of theoretical density was heat-treated for various times in the temperature range 700 to 790 °C to stimulate eutectoid decomposition below the eutectoid temperature (818 °C). Hardness and toughness were evaluated by the indentation method. The heat-treated material is significantly harder than pure ZnS, but the fracture toughness is about the same, although there is some evidence that toughness increases at longer reaction times.

INTRODUCTION

ZnS has been used commercially as an infrared (IR) window material for many years because of its good transmission in the range 0.4 to 12 μm. However, its fracture toughness, thermal shock resistance and erosion resistance need to be improved for applications in hostile environments, such as those encountered during missile operation. Many attempts have been made to explore the use of other IR-transmitting materials, but so far none has been found to possess a better overall combination of mechanical and optical properties than ZnS. Nevertheless, there is considerable room for improving the mechanical behavior of ZnS, and we are exploring methods to both strengthen and toughen it.

It is well known that additions of dispersions of particles of a second phase can strengthen materials and often toughen them. For instance, precipitation hardening has been for many years the main strengthening method for almost all the wrought aluminum alloys in use today. Also, the transformation toughening of ZrO_2 is assisted by a precipitation reaction; this is the most dramatic example of toughening of a ceramic material.

For optical materials it is also necessary to preserve their optical transmission characteristics after particles of a second phase have been introduced. These can induce losses due to absorption and scattering. Absorption losses can be controlled by selecting a second phase having good intrinsic IR transmittance, while scattering losses can be reduced if the average size of the second phase particles is

kept much smaller than the wavelength of the incident IR radiation. Fortunately, small particle sizes are also preferred for improved mechanical properties.

In order to strengthen and toughen ZnS ceramics by a dispersion of precipitates, it is first necessary to select a suitable "alloying" addition, then optimize the average size and volume fraction of the dispersion. This is done by controlling the percentage of the alloying component and experimenting with the subsequent heat treatments. Based on a search of the literature, the ZnS-CdS and ZnS-Ga_2S_3 systems were selected for initial study, with the latter system appearing to provide the greater promise because of the reported eutectoid reaction [1]. We have recently confirmed the existence of this reaction [2], wherein a mixture of the wurtzite form of ZnS containing 16 mol % Ga_2S_3 decomposes to cubic ZnS (sphalerite) and the tetragonal thiogallate phase $ZnGa_2S_4$ below 818 °C. $ZnGa_2S_4$, which crystallizes in the tetragonal $I\bar{4}2m$ structure, is a good IR-transmitting material in the range 2.5 to 12 μm [3,4]. Its unit cell parameters are $\mathbf{a}_t$ = 0.5297 nm and $\mathbf{c}_t$ = 1.0363 nm [4]. The lattice mismatch with cubic ZnS ($\mathbf{a}$ = 0.541 nm) is small, and the microhardness of $ZnGa_2S_4$ is comparable to that of ZnS [5]. It is also apparent, that precipitation from supersaturated solid solution can possibly be utilized to produce tougher and stronger ceramics at lower concentrations of Ga_2S_3. These potentially useful heat treatments are illustrated in Fig. 1 on the recently established phase diagram [2]. We report here for the first time the results obtained on the hardness and toughness of material of eutectoid composition.

EXPERIMENTAL PROCEDURES

Pure ZnS and ZnS-Ga_2S_3 solid solutions are prepared by solid-state sintering of measured amounts of the compounds in a flowing H_2S atmosphere at 925 °C for approximately 24 hr. This process always produces wurtzite solid solutions, as determined from x-ray diffraction. The sintered compacts are ground for about 1 hr using a mortar and pestle, producing a powder with an average particle size of about 1 μm. It was found that moisture adsorbed on the starting powders prevented the preparation of samples of high quality, imparting a gray color to specimens compacted under high pressure. Hence, a two-step process has been adopted to eliminate contamination by H_2O.

The powders are now initially cold-pressed in vacuum, heated to 850 °C and held for 20 min. This removes the water and partially sinters the pellet. The specimens are then cooled to room temperature and reheated to the hot-pressing temperature. The samples so obtained show almost no evidence of contamination. They are prepared by cold pressing at 7000 psi (48.3 MPa), followed by hot-pressing under 15000 psi (103.4 MPa) in a molybdenum die. The best densities that have been attained, relative to the theoretical density, are 95.5 % at 850 °C and 99.0 % at 900 °C. Alloys in this system containing as much as 50 mol % Ga_2S_3 have been prepared, but the mechanical properties to date have been evaluated only for pure ZnS and material of eutectoid composition (16 mol % Ga_2S_3).

To investigate the effect of heat-treatment conditions, the hot-pressed samples are encapsulated under vacuum in sealed silica ampoules, annealed at 920 °C for three days and cooled directly to aging temperatures in the range 700 to 790 °C to stimulate the eutectoid decomposition reaction. The progress of the reaction is followed by x-ray diffraction, monitoring the intensities of various diffraction peaks that can be assigned uniquely to the individual phases (many crystallographic planes in these structures have nearly the same interplanar spacings so that their peaks overlap). It turns out that eutectoid decomposition in this system is extremely sluggish. However, the eutectoid reaction exhibits classic "C-curve" behavior, with a maximum reaction rate at ~770 °C.

Hardness and toughness have been evaluated so far by the indentation method [6], using a Vickers microhardness indenter. The reacted samples are mounted and mechanically polished to a smooth finish using 0.3 μm Al_2O_3 grit as the final step. Typical indentations in pure ZnS and a sample of the 16 mol % Ga_2S_3 alloy are shown in Fig. 2. ZnS exhibits well-behaved patterns with clear, straight cracks emanating from the corners of the square indentation (Fig. 2a). The crack pattern in the alloy, on the other hand, is more irregular, the cracks often curving, branching and deviating from the plane intersecting the corners of the indentation. Also, at higher applied loads, P, material tends to spall near the corners of the indentations, a phenomenon that has not been observed in pure ZnS. The consequence of this is that there are larger uncertainties in the measurements made on the alloy than on pure ZnS.

The hardness, H, in GPa, is determined from the size, a, of the indentation, using the relationship

$$H = \frac{18.17\,P}{a^2} \tag{1}$$

where P is measured in kg and a in millimeters. The plane-strain fracture toughness, K_{Ic}, is calculated from the equation [6,7]

$$K_{Ic} = I\left(\frac{E}{H}\right)^{1/2} \frac{P}{C^{3/2}} \tag{2}$$

where I is a constant (~ 0.016), E is Young's modulus and C is the crack length. In principle, equation (2) provides a reasonable estimate of K_{Ic} for ZnS [7], but in our case an absolute measure is not possible because E is not known for the alloy and we have not yet measured it. Since Young's modulus of pure ZnS and the eutectoid alloy can be expected to differ, a comparison between these two materials is semiquantitative, at best.

However, the effect of heat treatment can be measured meaningfully because E is not likely to be strongly influenced by differences in the eutectoid mi-

crostructures. To this end we compare measurements of the "effective" fracture toughness, K', defined by the equation

$$K' = \frac{1}{I}\left(\frac{H}{E}\right)^{1/2} K_{Ic} \tag{3}$$

This quantity is the slope of a plot of P *vs* $C^{3/2}$, which follows from equation (2). Clearly, K' is proportional to K_{Ic}. Average values of C were computed for each sample from six indentations at three different loads. In all cases the indenter was in contact with the sample for 15 s. Since H is proportional to the density in both pure ZnS and the alloys, comparisons between these two groups of materials are best made on samples having nearly the same density.

RESULTS AND DISCUSSION

The hardness and percentage of theoretical density for representative hot-pressed samples (prior to heat treatment) are summarized in Table 1. It is apparent that the density of the samples increases with increasing hot-pressing temperature, and that H increases strongly with increasing density. This is not surprising, since it is known that porosity adversely affects hardness.

Representative data on the variation of H as a function of transformation time, t, at 790 °C are shown in Fig. 3 for material 97.4 % of theoretical density. The hardness increases initially, then levels out at a nearly constant value, which is considerably larger than that of pure ZnS of comparable density (95.6%).

A plot of the average value of C, raised to the 3/2 power, as a function of P is shown in Fig. 4 for the alloy transformed at 790 °C for four days. The data obey the linear relationship for a median crack system [6] and validate the use of equation (2). The slope of the curve in Fig. 4 provides a direct measure of K', enabling direct comparison of the fracture toughness as a function of t. The values of K' are shown as a function of t in Fig. 5. Within the limits of experimental error there is no clear-cut systematic dependence of K' on t, although there seems to be a trend towards a gradual increase in K' with increasing t at longer times.

This trend was also observed in other samples. One example, taken from material hot-pressed to 99 %ρ and transformed at 770 °C is shown in Fig. 6. The data are quite limited here because the hot-pressed disk was more brittle than the others, and only a limited number of samples could be extracted for indentation measurements. Nevertheless, the same trend as in Fig. 5 is observed, namely that K' appears to be increasing with increasing t.

These initial results suggest that the eutectoid decomposition reaction leads to improvements in mechanical behavior of the ZnS-based material. X-ray

diffraction of the 99% dense sample clearly indicates that the wurtzite phase, the starting phase for the decomposition reaction, disappears substantially with increasing t. This is shown in Fig. 7, where the intensities of the $\{10\bar{1}0\}$ and $\{10\bar{1}1\}$ wurtzite peaks decrease significantly after transformation times of 15 and 30 days at 770 °C. The disappearance of the wurtzite phase must be associated with increasing amounts of the sphalerite and tetragonal phases. It is interesting to note that although the volume fraction of these reaction products increases with transformation time, neither H nor K_{Ic} of the eutectoid-composition ceramic are affected. Nonetheless, the presence of the reaction products seems to influence the mechanical behavior. The eutectoid alloy exhibits a substantial increase in H (Fig. 3) but, based on equation (2), a concomitant decrease in K_{Ic} is expected. The fact that K_{Ic} exhibits no decrease (and possibly increases, as shown in Fig. 6) is an indication that the decomposition products impede crack propagation. The manner in which this occurs is not yet known, but a TEM study of this material is in progress to further improve our understanding of the microstructure/property relationships in these ceramics.

ACKNOWLEDGEMENT

The authors are grateful to the Office of Naval Research, Contract No. N00014-87-K-0531, for their financial support of this work. The assistance of Drs. D. Kipp and T. Vanderah of the Naval Weapons Center, China Lake, CA, in the preparation of the 16 mol % Ga_2S_3 powders is greatly appreciated.

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Table 1. Vickers hardness, H, and percentage of theoretical density, %ρ, as a function of the hot-pressing temperature, T_p.

T_p	%ρ	H (GPa)
850	94.4	2.91
850	95.5	3.55
900	97.4	3.64
900	98.8	4.42
900	99.0	4.54

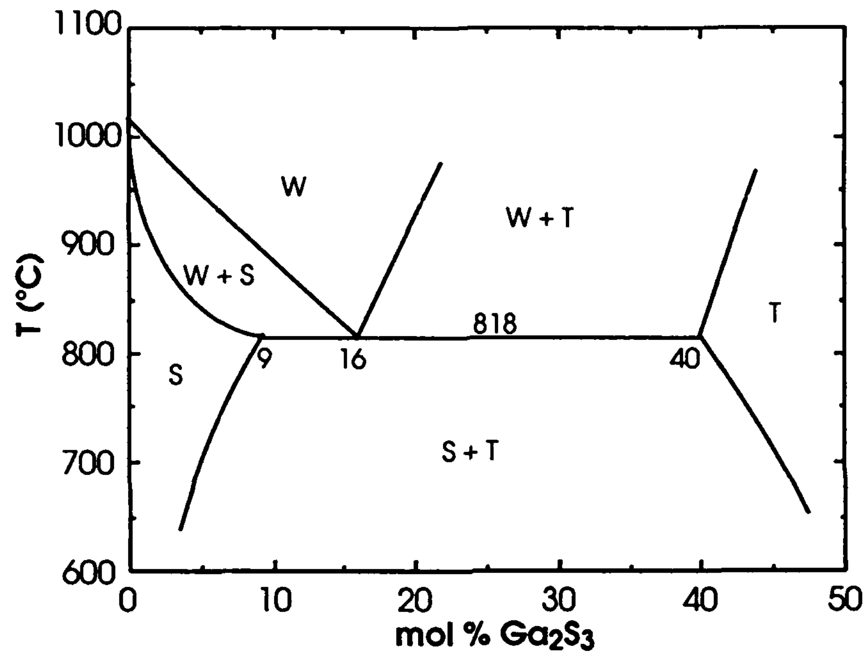

FIG. 1 Phase diagram of the ZnS-rich end of the ZnS-GaS3 system [2].

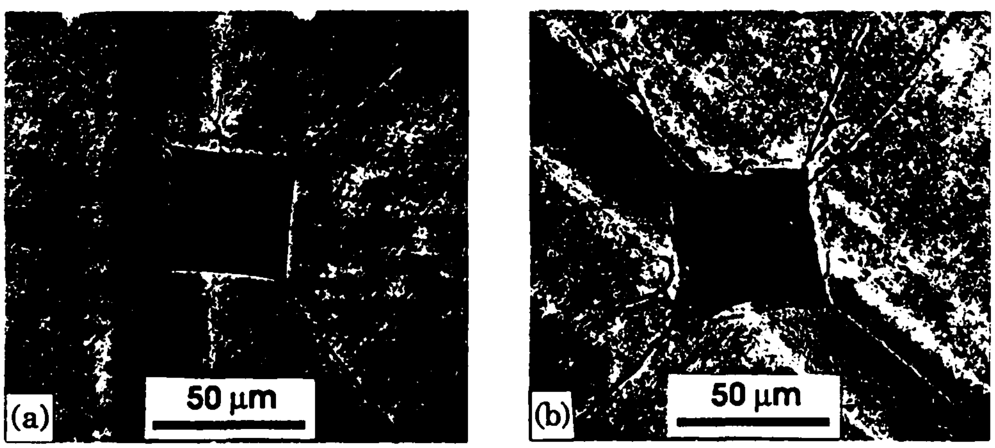

FIG. 2 Vickers hardness indentations under a load of: (a) 500 g for pure ZnS; (b) 1 kg for ZnS-16 mol % Ga_2S_3, both materials as-hot pressed.

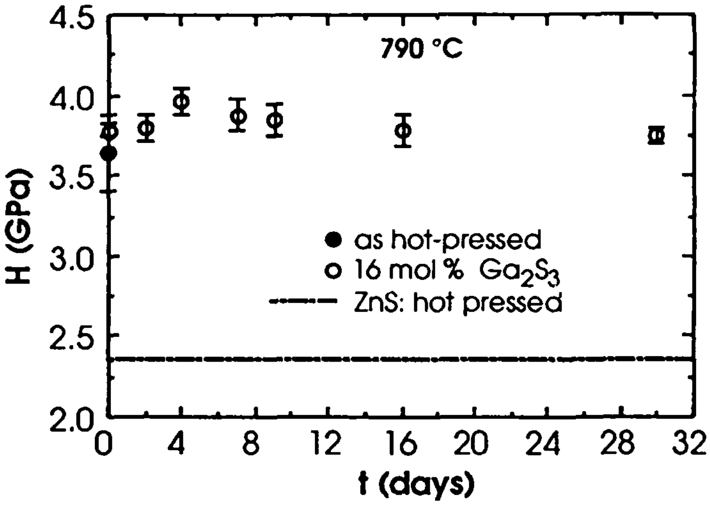

FIG. 3 Vickers hardness, H, as a function of transformation time, t, at 790 °C for the 16 mol % alloy of 97.4 % theoretical density.

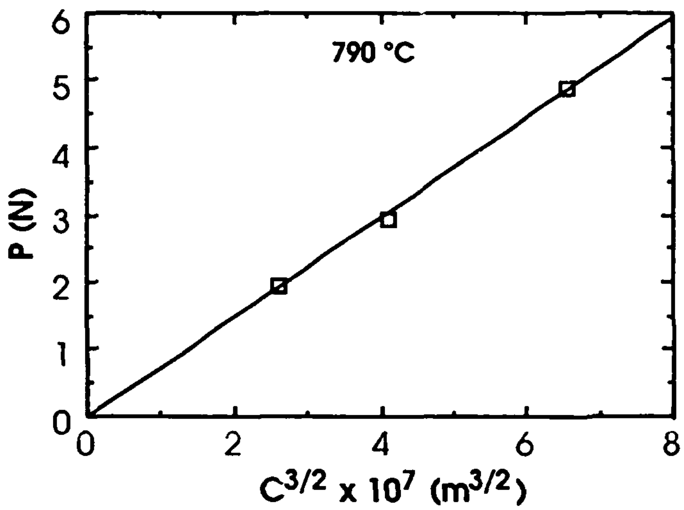

FIG. 4 Indentation load, P, *vs* the 3/2 power of the crack length, C, for the 16 mol % alloy transformed at 790 °C for 4 days.

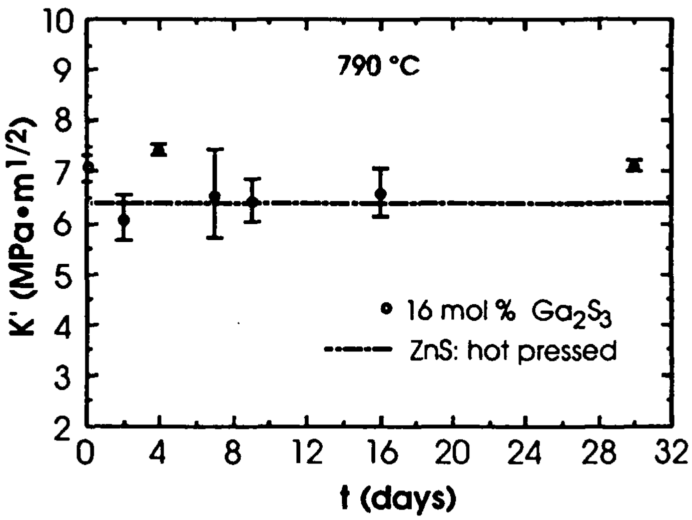

FIG. 5 Variation of the "effective" fracture toughness, K', as a function of transformation time, t, at 790 °C for the 16 mol % alloy of 97.4 % theoretical density.

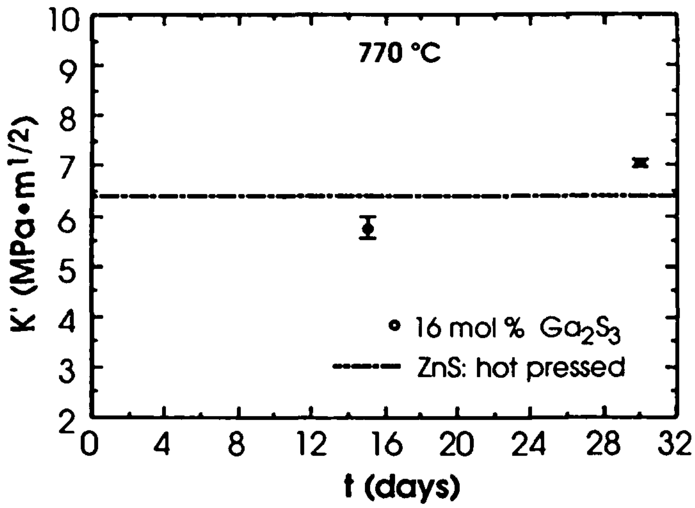

FIG. 6 Variation of the "effective" fracture toughness, K', as a function of transformation time, t, at 770 °C for the 16 mol % alloy of 99.0 % theoretical density.

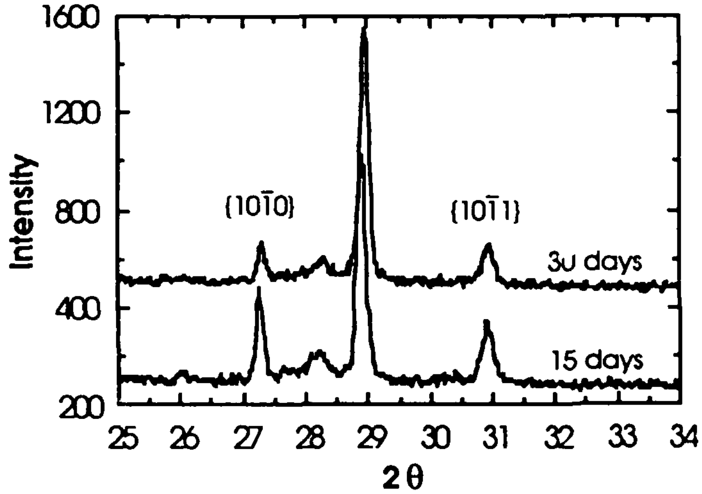

FIG. 7 Comparison of the intensities of the $\{10\bar{1}0\}$ and $\{10\bar{1}1\}$ wurtzite peaks in the 99.0 % dense sample after transformation times of 15 and 30 days at 770 °C.